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Authors:

Thomas P. Dorchak (DOE/METC)
Santosh K. Gangwal (Research Triangle Institute)
Brian S. Turk (Research Triangle Institute)

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Santosh K. Gangwal and Brian S. Turk
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194

Thomas P. Dorchak
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880

ABSTRACT

Regenerable metal oxide sorbents, such as zinc titanate, are being developed to efficiently remove hydrogen sulfide (H_2S) from coal gas in advanced power systems. Dilute air regeneration of the sorbents produces a tailgas containing a few percent sulfur dioxide (SO_2). Catalytic reduction of the SO_2 to elemental sulfur with a coal gas slipstream using the Direct Sulfur Recovery Process (DSRP) is a leading first-generation technology. Currently the DSRP is undergoing field testing at gasifier sites. The objective of this study is to develop second-generation processes that produce elemental sulfur with limited use of coal gas. Novel approaches that were evaluated to produce elemental sulfur from sulfided sorbents include (1) SO_2 regeneration, (2) substoichiometric oxidation, (3) steam regeneration followed by H_2S oxidation, and (4) steam-air regeneration. Experimental results at high temperature and high pressure demonstrate that, with simple sorbent modifications, direct regeneration to elemental sulfur is feasible without the use of coal gas.

INTRODUCTION

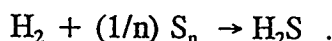
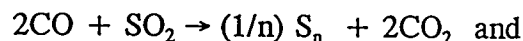
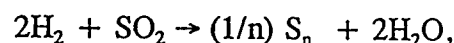
Hot-gas desulfurization research is focused on air-regenerable mixed-metal oxide sorbents such as zinc titanate and zinc ferrite that can reduce the sulfur in coal gas, present

primarily as H_2S , to <20 ppmv and that can be regenerated in a cyclic manner with air for multicycle operation.

The sulfidation/regeneration cycle can be carried out in fixed-, moving-, and fluidized-bed reactor configurations. The regeneration reaction is highly exothermic, requiring the use of large volumes of diluent to control the temperature and results in a dilute SO_2 -containing tailgas that must be further treated. Under contracts with the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC), many approaches have been evaluated for treatment of the tailgas. These include adsorption of SO_2 using calcium-based sorbents followed by landfilling of calcium sulfate as well as conventional methods such as Wellman-Lord coupled with high-temperature syngas reduction and augmented Claus for converting the SO_2 to elemental sulfur. Two advanced approaches that DOE/METC is currently sponsoring include the General Electric (GE) moving-bed process and the DSRP, both of which convert the SO_2 tailgas to a useful byproduct. Economic evaluations of these two approaches, conducted by Gilbert Commonwealth, for DOE show they are very closely competitive, with costs within 1 percent of each other, cost of electricity basis.

In the GE moving-bed process (Cook et al., 1992), the H_2S in coal gas is removed by moving a bed of sorbent countercurrent to the upward gas flow. The sulfided sorbent is transferred to a moving-bed regenerator below the moving-bed absorber using a lock-hopper arrangement. In the regenerator, SO_2 recycle is used to control the exothermicity of the reaction of the sulfided sorbent with air as well as to produce an SO_2 tailgas containing 10- to 13-vol% SO_2 . The regenerated sorbent is lifted back to the absorber using a bucket elevator arrangement. The 10- to 13-vol% SO_2 is a suitable feed for a sulfuric acid plant.

In the DSRP (Dorchak et al., 1991; Gangwal et al., 1993), the SO₂ tailgas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the high-temperature, high-pressure (HTHP) conditions of the tailgas and coal gas. The stoichiometry of the reactions is



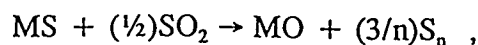
Recent results indicate that >99 percent selectivity to elemental sulfur can be achieved in a single stage by carefully controlling inlet stoichiometry to maintain a reducing gas (H₂ + CO) to SO₂ mole ratio of 2.0.

The strength of the GE moving-bed process stems from producing a useful byproduct during regeneration, whereas the strength of the DSRP is the elemental sulfur byproduct.

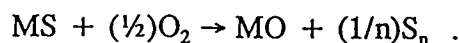
Combining production of an elemental sulfur byproduct and sorbent regeneration in an economically competitive process with reduced coal gas consumption would represent a significant improvement in hot-gas desulfurization technology. Efficient development of a process fulfilling these requirements would focus research efforts not only on the most promising reaction/process, but with the most promising sorbent and operation conditions. This paper presents a critical evaluation of reaction/process schemes identified with the potential to produce both a regenerated sorbent and elemental sulfur byproduct without or with limited use of coal gas and some preliminary empirical results.

ALTERNATIVE REACTION/PROCESS SCHEMES

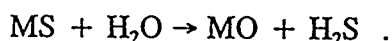
Two alternative regeneration reactions producing elemental sulfur are SO₂ regeneration and partial oxidation. The reaction for SO₂ regeneration is



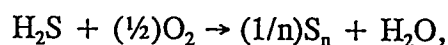
where MS represents a metal sulfide and MO represents a metal oxide. Partial oxidation is represented by



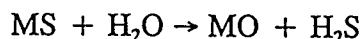
A third regeneration reaction readily incorporated into a process producing elemental sulfur is steam regeneration. For steam regeneration the reaction is



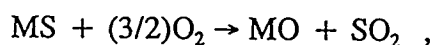
Conversion of H_2S to elemental sulfur could be performed by direct oxidation,



in a separate reactor. During development of DSRP, direct oxidation of H_2S at HTHP conditions in the presence of a suitable catalyst was rapid and achieved high conversions (Gangwal et al., 1992). Alternatively, if a small fraction of oxygen were added to the regeneration steam, regeneration reactions,



and



and a sorbent-catalyzed augmented Claus reaction,



could be performed in a single reaction vessel. However, reaction conditions and sorbent compositions must be carefully selected to allow competing reactions while maintaining a high reaction rate for the sulfur producing reaction.

REACTION/PROCESS EVALUATION

Based on a concept assessment, alternative reaction/process schemes listed in order of increasing potential are partial oxidation, simultaneous steam and air regeneration, steam regeneration with direct oxidation of H_2S , and SO_2 regeneration.

Partial oxidation is attractive due to lack of thermodynamic limitations, thereby allowing the choice of sorbent purely on its ability to remove H_2S . The challenge is to inhibit the rapid sorbent-catalyzed oxidation of elemental sulfur to SO_2 as sulfur emerges from the sorbent. Possible remedies include reducing reaction rates by reducing temperature, limiting the oxygen supply, and reducing sorbent and sulfur contact. Lower temperatures also reduce the rate sulfur vapor diffuses out of the sorbent increasing contact time between sulfur and the sorbent. Although the concept of supplying sufficient oxygen to promote sulfur formation, but not enough to allow subsequent oxidation to SO_2 , is simple to envision, it is extremely difficult to achieve even in complex reactor designs. Reducing contact time between sorbent and sulfur can be accomplished with complex reactor designs and sorbent modification. Sorbent modification would require increasing pore sizes, while simultaneously reducing surface area and increasing mechanical strength. Development of a partial oxidation process to produce a regenerated sorbent and elemental sulfur faces many challenging technical barriers.

The use of steam for regeneration involves a reaction that is simply the reverse of the sulfidation reaction. Consequently, any sorbent capable of removing H_2S down to parts-per-million levels will only release parts-per-million levels of H_2S during steam regeneration. The H_2S release will increase with steam concentration but only weakly (e.g., linearly, depending on sorbent stoichiometry). Higher steam concentrations and temperatures assist

the regeneration but could result in severe sorbent sintering. Additional technical problems associated with steam regeneration are (1) effective condensation of sulfur occurs at a lower temperature than steam at HTHP, (2) large heat duty is required to generate steam from condensed process steam or fresh water, and (3) treatment of wastewater containing SO_2 and H_2S is expensive. Simultaneous steam and air regeneration will require expensive corrosion-resistant equipment as mixtures of steam and SO_2 are corrosive.

Equilibrium constraints limit both sulfur production and sorbent regeneration for SO_2 regeneration as can be seen for several iron- and zinc-based sorbents in Table 1. Although the trends visible in Table 1 indicate strong SO_2 regeneration and high levels of H_2S removal are mutually exclusive, the unique requirements of SO_2 regeneration may provide a strategy to overcome this problem. As SO_2 regeneration is endothermic, SO_2 regeneration will require additional heat and SO_2 to sustain the regeneration. Oxygen regeneration, which is rapid and exothermic, produces both heat and SO_2 . Carefully balancing components from the upper and lower portions of Table 1 may produce a sorbent capable of reducing H_2S levels to very low levels and provide enough SO_2 and heat from oxygen regeneration to complete regeneration with SO_2 , converting all sulfur species to elemental sulfur. One particular process involving SO_2 and O_2 regeneration, among many considered, is shown in Figure 1. Since SO_2 regeneration is slow, it may be necessary to increase reaction temperatures to obtain necessary rates. Higher reaction temperatures also produce more favorable equilibrium conditions for SO_2 regeneration. Maximum regeneration temperatures will be fixed by sorbent sintering, materials of construction available for reactor and process equipment, and process heat integration.

Regeneration with SO_2 could also increase sorbent life, allow simple extraction of ele-

Table 1. Thermodynamic Calculations for Sulfidation and SO₂ Regeneration

Sorbent	Sulfidation Equilibrium H ₂ S Concentration with 20% Steam at 800 K (ppm)	Equilibrium Constants for SO ₂ Regeneration			
		800 K		1,000 K	
		S ₂ (×10 ⁻⁴)	S ₈ (×10 ⁻⁴)	S ₂ (×10 ⁻⁴)	S ₈ (×10 ⁻⁴)
ZnO	3	0.17	0.51	3.3	1.1
ZnO•TiO ₂	3	0.19	0.56	3.7	1.2
FeO	107	6.2	19.0	55.0	18.0
ZnO•Al ₂ O ₃	1,055	61.0	183.0	316.0	100.0
FeO•Al ₂ O ₃	3,484	202.0	605.0	717.0	227.0

mental sulfur byproduct, and reduce corrosion. With SO₂ regeneration, sulfate formation, a major cause of sorbent decrepitation, does not occur. Absence of sulfate formation during SO₂ regeneration should maintain mechanical stability extending life expectancy for sorbents. Since dry SO₂ is much less corrosive than an SO₂ and steam mixture, corrosion with SO₂

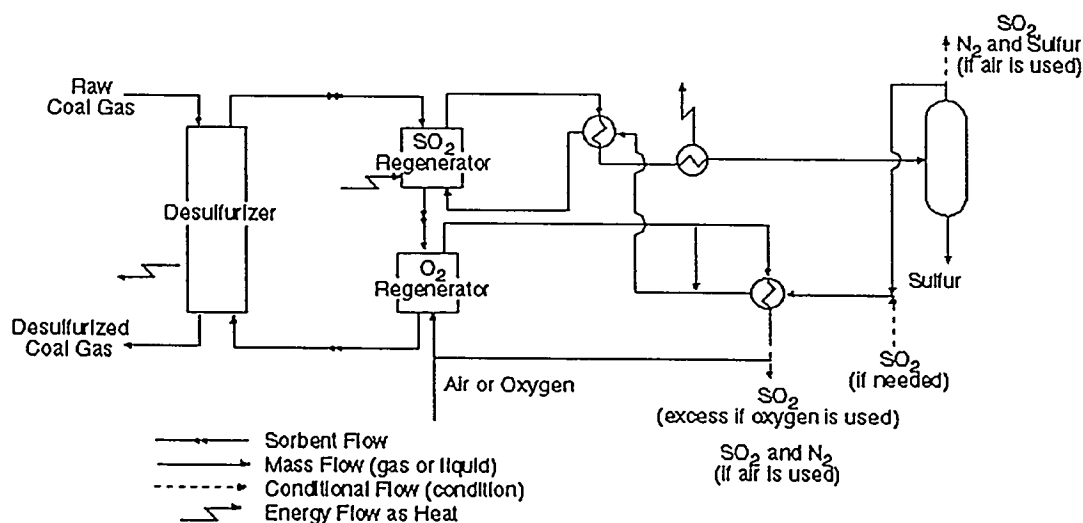


Figure 1. Three Reactor Systems for SO₂ Regeneration Followed by O₂ Regeneration

regeneration should be minimal. However, development of a viable process hinges on achieving sufficient heat integration and sorbent optimization to obtain an economically competitive process. Based on a smaller number of barriers, SO_2 regeneration offers a greater potential for rapid process development than other alternative reaction/process scheme.

Sorbent Metal-Oxide Selection

A number of sorbent metal-oxide formulations were assessed for feasibility according to information gleaned from a literature search and thermodynamic calculations. A review of the literature indicated sorbents based on oxides of copper, cerium, manganese, cobalt, tin, iron, and zinc individually and in combinations have been associated with elemental sulfur production during regeneration. These metal or mixed-metal oxides have been investigated both without as well as combined with a secondary oxide, typically silica, alumina, titania, and chromia. The roles of these secondary oxides include support for strengthening mechanical structure, as stabilizers against reduction of the metal oxide to metal in a reducing environment, and/or as modifiers of thermodynamic properties of the metal oxide to enhance elemental sulfur formation during regeneration. Based on these evaluations, sorbents based on copper, cerium, cobalt, and tin as the principal metal oxides were found to be poor desulfurizing agents, costly, or not easily regenerated with SO_2 , or they had a combination of these deficiencies. Thus, they were eliminated from further consideration. Of the remaining metal oxides, namely oxides of manganese, iron, and zinc, due to the similarity of reduction and desulfurizing properties of manganese and iron, iron was chosen for further consideration because more is known about iron. Also zinc remained a candidate for further consideration due to its very high desulfurization efficiency even though it showed

very poor thermodynamics for SO₂ regeneration. In combination with iron, zinc could act as a polishing agent for H₂S which could be regenerated using air to produce SO₂ needed for SO₂ regeneration. Thus, this work has concentrated on iron- and zinc-based sorbents.

TESTING APPARATUS

Laboratory experiments to test the SO₂ regeneration concept were carried out using an atmospheric pressure thermogravimetric analyzer (TGA), a high-pressure TGA, and a high-pressure lab-scale reactor. The high-pressure lab-scale reactor system is shown in Figure 2. The reactor is made of a ½-in. stainless steel tube capable of operation at 750 °C and 200 psig. Provision is made for reducing the sorbent with H₂S-free coal gas, sulfiding the sorbent with simulated coal gas, or regenerating the sorbent with up to 15 vol% SO₂. The gas exiting the reactor is passed through heated tubing into a 130 °C convective oven where a 0.1-μm filter is used to collect sulfur. The exit gas sample can be analyzed by gas chromatography (GC) to measure H₂S breakthrough and vented through a back pressure regulator. Cyclic atmospheric pressure and high-pressure TGA experiments were carried out using simulated coal gas for sulfidation and up to 15 vol% SO₂ for regeneration. The concept of SO₂ regeneration followed by air regeneration was also evaluated.

RESULTS

A number of sorbents based on iron and zinc oxides were prepared and tested for SO₂ regeneration using the TGAs and the laboratory reactor system. The benchmark zinc titanate and zinc ferrite sorbents were ZT-4 and L-7. These sorbents have been developed for fluidized-bed desulfurization incorporating air regeneration under a previous DOE contract. The ZT-4 sorbent (based purely on ZnO as the active sorbent) and other ZnO-only-based sorbents showed essentially no regeneration with 3.3 percent SO₂ in N₂ at up to 800 °C and

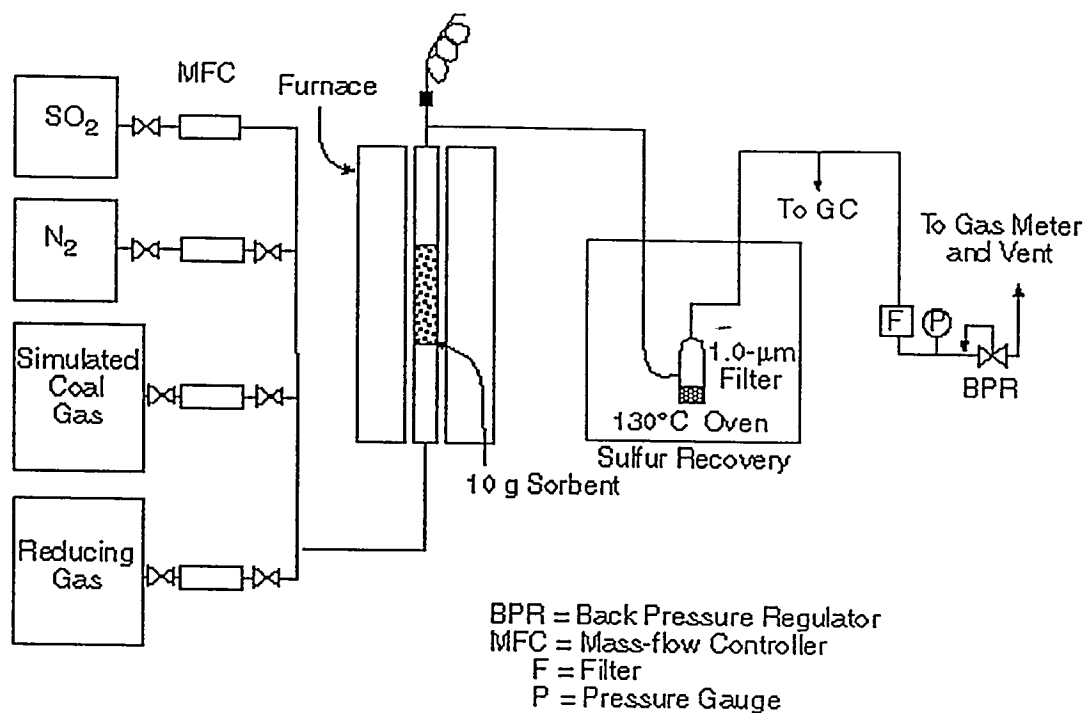


Figure 2. Laboratory-Scale SO₂ Regeneration Test System

10 atm. However, iron- and zinc-iron-based sorbents showed good regeneration with SO₂. The rates of regeneration of the various sorbents depended on how they were prepared. Due to the proprietary nature of the preparations, no data related to the sorbent's preparation or pore structure are presented. Average regeneration rates (expressed in terms of sulfur production rate) are presented in Table 2 along with average sulfidation rates and conditions. The sulfidations were conducted using a simulated coal gas containing 0.5 vol% H₂S. The results suggest that SO₂ regeneration is a feasible approach for iron-based sorbents. Significant potential for increased SO₂-regeneration rate is possible by increasing the SO₂ concentration and by modifying sorbent properties.

The L-7, R-2, and R-5 sorbents did not show complete regeneration in SO₂ because the zinc portion of the sorbent did not regenerate. The iron-only-based sorbents completely

Table 2. Comparison of Sulfidation and SO₂ Regeneration for Several Sorbents
(3.3 percent SO₂, 10 atm)

Sorbent Designation	Sorbent Type ^a	Temperature (°C)		Sulfidation Rate (×10 ⁻⁴) (g sulfur/g sorbent/min)	Regeneration Rate (×10 ⁻⁴) (g sulfur/g sorbent/min)
		Sulfidation	Regeneration		
L-7	Zn+Fe	550	800	10.8	2.0
RTI-3	Fe+P	450	800	19.2	18.2
FE-90	Fe	400	800	34.0	4.6
R-2	Zn+Fe	550	700	24.0	2.2
R-3	Fe+P	500	700	3.8	5.8
R-4	Fe+P	500	700	2.0	4.4
R-5	Zn+Fe+P	460	700	13.4	4.4

^a P = Proprietary additive.

regenerated in SO₂. To test the potential of SO₂ regeneration (with higher SO₂ concentrations) followed by air regeneration for zinc-iron-based sorbents, the R-5 sorbent was subjected to three cycles at 10 atm, each consisting of a sulfidation at 460 °C, a SO₂ regeneration with 3.3 to 15 percent SO₂ at 650 to 700 °C, and finally an air regeneration with 2 percent O₂ at 700 °C.

The sorbent showed consistent behavior over the three cycles of operation. The rates of sulfidation, SO₂ regeneration, and air regeneration are compared in Table 3. Results show that, as SO₂ concentration is increased, SO₂-regeneration rates increased. Since both temperature and SO₂ concentration influence regeneration rates, it should be possible to optimize regeneration rates at a desirable temperature by adjusting SO₂ concentration.

Laboratory-scale tests of SO₂ regeneration were carried out with the R-5 sorbent.

About 5 g of the sorbent was loaded in the reactor and fully sulfided using simulated coal gas. SO₂ regeneration was then started at 7.8 atm and 700 °C with 15 percent SO₂ in N₂. Samples were withdrawn after 5.5 h and 10 h of regeneration for TGA analysis. The TGA analysis showed, as expected, that the zinc portion of the sorbent was not regenerated. However, the iron portion of the sorbent regenerated at a rate of 2.1×10^{-4} (g sulfur/g sorbent/min). This result is in the ballpark of TGA results presented in Table 3 at 10 atm. After 10 h of operation, sulfur plugging downstream of the reactor occurred. The sulfur was removed and examined. It was found to be yellow without any kind of odor.

SUMMARY

Four approaches to the production of elemental sulfur during the regeneration of sulfided metal sorbents were evaluated: (1) SO₂ regeneration; (2) substoichiometric oxidation; (3) steam regeneration followed by H₂S oxidation; and (4) steam-air regeneration. The first approach, SO₂ regeneration, appeared to have the least technical or engineering challenges when using iron- and zinc-containing sorbents. Laboratory studies were carried out using an

Table 3. Comparison of Sulfidation, SO₂-Regeneration, and Air-Regeneration Rates for R-5 Sorbent (pressure = 10 atm)

Reactant	Temperature (°C)	Rate ($\times 10^{-4}$) (g sulfur/g sorbent/min)
Simulated Coal Gas (0.5% H ₂ S)	460	13.4
SO ₂		
3.3%	700	4.4
3.3%	650	0.22
15%	650	3.7
2% O ₂ in N ₂	700	5.0*

* Result probably limited by mass transfer.

atmospheric TGA, a high-pressure TGA and a high-pressure, small lab-scale reactor. The iron component could be completely regenerated at rates comparable to oxidation with dilute oxygen in the fixed-bed reactor. The results suggest that SO₂ regeneration may be feasible.

FUTURE WORK

Feasibility needs to be confirmed at a larger scale, permitting material balances, particularly in regard to sulfur species. A larger, 2-inch diameter reactor is now assembled at RTI's laboratory. Testing is currently underway. Laboratory scale and TGA experiments will continue in hopes of optimizing processing conditions and/or sorbent composition. A catalyst vendor is producing sorbent samples for testing purposes.

LITERATURE CITED

- Cook, C.S., et al. 1992. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System." In *Proceedings of the 12th Annual Gasification Gas Stream Cleanup Systems Contractors' Review Meeting*. Vol. 1, DE93000228, p. 84.
- Dorchak, T.P., et al. 1991. "The Direct Sulfur Recovery Process." *Environmental Progress* 10(2):68.
- Gangwal, S.K., et al. 1992. "The Direct Sulfur Recovery Process for Refinery Gas Processing." AIChE Meeting, New Orleans, March.
- Gangwal, S.K., et al. 1993. "DSRP, Direct Sulfur Production." In *Proceedings of the Coal-Fired Power Systems 93—Advances in IGCC and PFCB Review Meeting*. DOE/METC, Morgantown, WV. June.